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EFFECT OF THE TECHNOLOGICAL PARAMETERS ON THE PROPERTIES OF GRANULAR POROUS CRYSTAL GLASS MATERIAL BASED ON ZEOLITE-BEARING ROCK

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The effect of various technological parameters in the production of light porous granular crystal glass material based on zeolite-bearing rock is studied. To produce light porous crystal glass material at temperatures corresponding to the foam-glass production technology (800 – 900°C), the mix must be presintered at 700°C. It is found that increasing the fineness of the milling of the fritted mix to particles sizes smaller than 0.08 mm decreases the bulk density of the granular zeolite foam.

Increasing energy-carrier prices are giving a sense of urgency to the development of new, effective, porous, granular materials from raw materials which have not been previously used as well to the development of low-temperature technologies for producing them. An alternative, natural, raw-materials source for the production of porous heat-insulating materials is zeolite-bearing rock, which has the ability to swell at high temperatures (1100 – 1200°C) and form a porous cellular structure [1, 2]. Our investigations have shown that adding fluxes to the mix permits decreasing the firing temperature of granular zeolite to 850°C [3, 4].

The effect of the fineness of the comminution of the raw materials mixture on the change of the properties of porous granular material based on zeolite-bearing rock and the effect of the duration and temperature of the presintered raw-material mix as well as the moisture content of the granules are investigated.

Zeolite-bearing rock from the Sakhaptinskoe deposit (Krasnoyarskii krai) was studied. This rock is exemplified by zeolite mineral (clinoptilolite and heulandite), quartz, feldspars, and clay materials (montmorillonite). The chemical composition of the zeolite-bearing rock is as follows (%[2]): 66.10 SiO_2, 0.34 TiO_2, 12.51 Al_2O_3, 2.36 Fe_2O_3, 2.27 CaO, 1.66 MgO, 1.04 Na_2O, 3.24 K_2O, and 10.28 other.

The comminuted zeolite-bearing rock was mixed with added soda. Then the mixture was fritted, after which the frit was milled and mixed with a gas-forming agent (glycerin). Granules were formed from the prepared mixture (with added water) on a plate granulator. Finally, the granules were foamed at 850°C.

Figure 1 shows the results of thermo-microscopic studies performed with a TS 1500 (Germany) high-temperature microscope. The size of the sample (particle taken from a granule) did not exceed 1 mm. The sample starts to sinter at 825°C, the particle shape becomes more rounded, and the particle size decreases somewhat. At 850°C the mass passes into a pyroplastic state, and the processes resulting in the release of the gas phase create the necessary condition for the formation of a porous structure.

The large specific surface area of the glass powder in the foam-forming mixture plays a decisive role in obtaining foam glass by means of the classical technology. A direct consequence of the structural changes of the glass surface is higher reactivity, which manifests during sintering of the glass powder as well as during the formation of the glass foam itself.

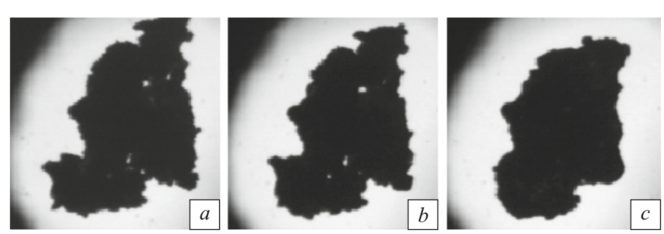

Fig. 1. Results of thermo-microscopic investigations of the raw material mixture with a gas-forming agent: temperature 23°C (*a*), 825°C (*b*), and 850°C (*c*).

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[2] Here and below — content by weight.

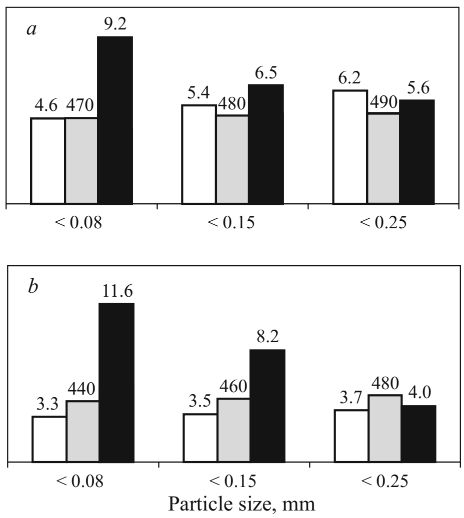

Fig. 2. Properties of granular zeolite foam fractions 5 mm (*a*) and 10 – 20 mm (*b*) as a function of the fineness of the comminution of the fritted mix: ☐) compression strength, MPa; ☐) bulk density, kg/m^3; ■) water absorption, %.

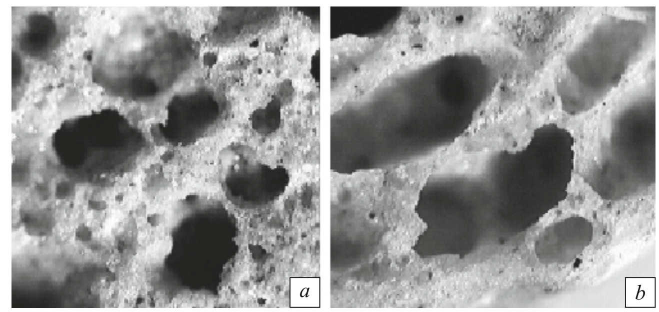

Fig. 3. Granular zeolite foam (× 20) obtained using frits with comminution fineness less than 0.25 mm (*a*) and less than 0.08 mm (*b*).

The sintering temperature of the glass powder depends on its specific surface area: the larger the area, the lower the temperature. For this reason, the effect of the fineness of the milling of the fritted mix, based on the zeolite-bearing rock, on the properties of the granular porous crystal glass material was studied. A synchronous thermal analysis of the raw material mixture, preformed using a SDT Q600 (USA) thermogravimetric analyzer, showed the following.

After the primary sintering the fritted mix contains an amorphous component. For this reason, when the granules foam up the mix starts to melt at lower temperature — 600°C. In the case of coarse comminution of the mix to particle size less than 0.25 mm, the mechanically bound moisture is removed at lower temperatures. The exothermal effect at 325 – 357°C corresponds to burnup of glycerin and release of CO_2. During heating, a mixture with particles smaller than 0.25 mm has an exothermal effect 149.6 J/g at 327°C. When the mix is comminuted to finer particles sizes (< 0.08 mm), all processes occurring during heating proceed with greater intensity: the exothermal effect in this case is 342.9 J/g.

Figure 2 displays the results of investigations of the properties of granular zeolite foam of different fractions as a function of the fineness of the comminution of the fritted mix.

Figure 3 shows zeolite foam granules made from fritted mix. A decrease of the size of the particles in the mix to 0.08 mm results in more active melting of the mixture and lower viscosity. As a result, a structure with larger pores forms and the thickness of the barriers between the pores decreases. The density and the strength of the granular zeolite foam decrease and water-absorption increases.

The temperature and duration of the presintering of the mix also affect the change in the properties of the granular zeolite foam (Table 1). The sintering of the raw material mixture at 600°C is inadequate to melt the mixture; in consequence, the granules obtained possess a fine-pore structure (Fig. 4).

X-ray phase analysis performed with a TT 3003/OED diffractometer made it possible to determine the composition of the main crystalline phase and the content of the glass phase in the mixture after sintering for 0.5, 1, and 2 h and finished zeolite foam samples (Table 2). It was determined that after the mixture is sintered at 700°C the main crystalline phases (about 30%) are quartz, feldspars, and diopside as well as a glass phase (about 70%). The holding time at the sintering temperature does not have a great effect on the

TABLE 1.

Preliminary fritting		Properties of granular zeolite foam					
		bulk density, kg/m^3		compression strength, MPa		water absorption, %	
temperature, °C	holding time, h	5 mm	10 – 20 mm	5 mm	10 – 20 mm	5 mm	10 – 20 mm
600	0.5	535	524	5.0	2.3	3.03	3.40
	1.0	523	447	5.8	2.7	3.30	4.70
	1.5	557	454	5.4	1.7	3.50	7.70
700	0.5	560	500	5.8	4.0	5.00	6.00
	1.0	553	480	6.2	3.7	5.30	5.60
	2.0	500	400	4.8	3.0	7.00	7.50
750	0.5	528	386	3.7	1.5	3.33	5.88

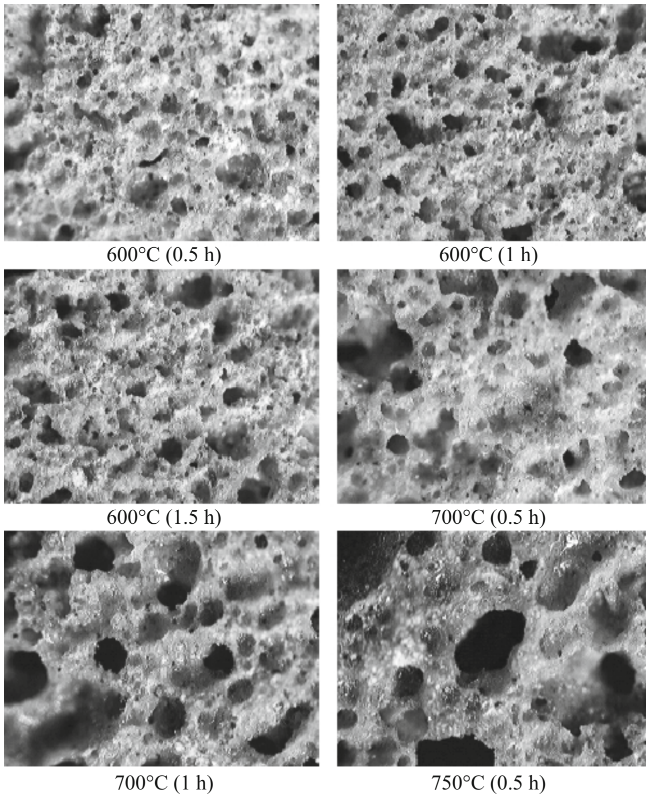

Fig. 4. Granular zeolite foam using frit sintered at different temperatures (× 20).

change of the phase composition of the mixture and the finished zeolite foam frit. Holding the mixture at the sintering temperature for 30 min is sufficient for 70% of the mixture to pass into an amorphous state. Foaming of shaped granules from the mixture consisting of 70% glass phase with a gas-forming agent added gives a porous cellular structure — an analogue of foam glass.

TABLE 2.

Main crystalline phases	Holding time during fritting (700°C), h	Phase content, wt. %	
		in the fritted mix	in the zeolite foam material
Quartz	0.5	7.58 ± 0.51	4.35 ± 0.39
Feldspars		18.10 ± 1.80	26.80 ± 3.60
Diopside		1.47 ± 0.75	5.84 ± 0.78
Amorphous component		72.76 ± 1.95	63.10 ± 3.30
Quartz	1.0	7.52 ± 0.57	3.79 ± 0.36
Feldspars		19.31 ± 2.20	20.39 ± 2.90
Diopside		2.61 ± 0.75	6.07 ± 0.81
Amorphous component		70.55 ± 2.19	69.76 ± 2.80
Quartz	2.0	8.27 ± 0.60	4.11 ± 0.42
Feldspars		18.58 ± 1.95	22.40 ± 3.30
Diopside		2.39 ± 0.75	5.16 ± 0.81
Amorphous component		70.76 ± 2.04	68.30 ± 3.30

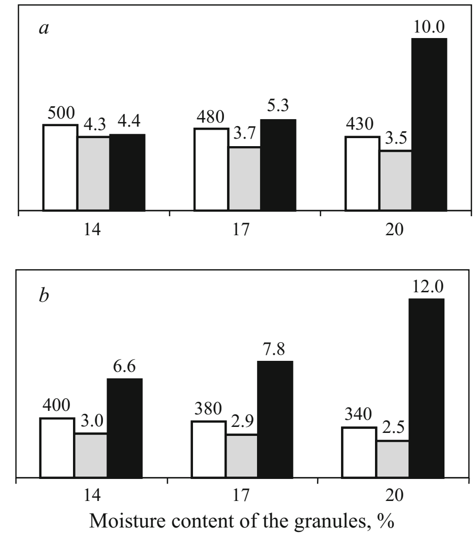

Fig. 5. Properties of granular zeolite foam fractions 5 mm (*a*) and 10 – 20 mm (*b*) as a function of the moisture content of the granules: □) bulk density, kg/m^3;) compression strength, MPa; ■) water absorption, %.

The moisture content of the granules is one of the important factors which affect their foaming (Fig. 5). Increasing the moisture content up to 20% results in greater water absorption by the granular zeolite foam; this is explained by additional gas release of the residual chemically bound water during foaming and an increase of the open-pore fraction. The bulk density decreases to 340 kg/m^3 and the strength also decreases. In addition, the high moisture content of the granules can cause them to adhere to one another during storage and shipment and weld junctions to form during sintering.

In summary, just as in the technology for producing glass foam, when producing a light porous crystal glass material based on zeolite-containing rock some of the main technological factors influencing the properties of a material are as follows: fineness of comminution of the fritted mix and the moisture content of the granules which are to be foamed. The moisture content of the granules formed must not exceed 20%, because at higher values of the moisture content the

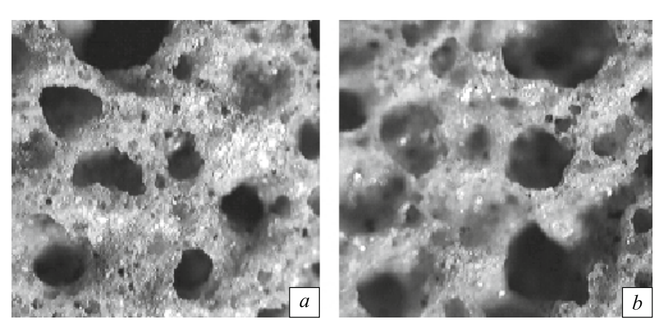

Fig. 6. Granular zeolite foam (× 20) with moisture content 14% (*a*) and 20% (*b*) in the granules at foaming.

granules adhere to one another and undergo deformation. Comminuting the frit mix to particle size less than 0.08 mm decreases the bulk density of the granular zeolite foam to 440 – 470 kg/m^3. To produce a light porous crystal glass material based on zeolite-containing rock at temperatures corresponding to the technology used to produce foam glass (800 – 900°C), the mix must be pre-sintered at 700°C in order for the silicate- and melting-forming processes to go to completetion (> 70% glass phase).

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